CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED NOTES OF CHAPTER -03)
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Electrochemistry

Gibbs Free Energy

The Gibbs free energy, originally called *available energy*, was developed in the 1870s by the American scientist Josiah Willard Gibbs. In 1873, Gibbs described this "available energy" as

the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition.

In the early days of chemistry, chemists used the term "affinity" to describe the force responsible for chemical reactions. In the modern era, affinity is called Gibbs free energy.

Definition

Gibbs free energy is a measure of the potential for reversible or maximum work that may be done by a system at constant temperature and pressure.

It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously at constant temperature and pressure. Gibbs free energy *G* is defined as

$G = H - TS$

Where *H*, *T*, and *S* are the enthalpy, temperature, and entropy

The *SI* unit for Gibbs energy is the kilo joule.

Changes in the Gibbs free energy *G* correspond to changes in free energy for processes at constant temperature and pressure.

The change in Gibbs free energy change is the maximum non-expansion work obtainable under these conditions in a closed system;

ΔG is negative for spontaneous processes, positive for non spontaneous processes, and zero for processes at equilibrium.

Gibbs free energy is also known as (G), Gibbs' free energy, Gibbs energy, or Gibbs function. Sometimes the term "free enthalpy" is used to distinguish it from Helmholtz free energy.

The terminology recommended by the International Union of Pure and Applied Chemistry (IUPAC) is Gibbs energy or Gibbs function.

Positive and Negative Free Energy

The sign of a Gibbs energy value may be used to determine whether or not a chemical reaction proceeds spontaneously. If the sign for *ΔG* is positive, additional energy must be input for the reaction to occur. If the sign for *ΔG* is negative, the reaction is thermodynamically favorable and will occur spontaneously.

However, just because a reaction occurs spontaneously doesn't mean it occurs quickly. The formation of rust (iron oxide) from iron is spontaneous, yet occurs too slowly to observe. The reaction:

$\mathbf{C}_{\mathbf{(s)}}^{\mathbf{diamond}} \rightarrow \mathbf{C}_{\mathbf{(s)}}^{\mathbf{graphite}}$ also has a negative *ΔG* at 25 C and 1 atmosphere, yet diamonds do not appear to spontaneously change into graphite.

SPONTANEITY OF REACTION

$OG = – nFE_{CELL}$

For a spontaneous cell reaction OG should be negative and cell potential should be positive.

If we take standard value of cell potential in the above equation we will obtain standard value of OG as well.

$OG^{o} = – nFE^{0}_{CELL}$

Types of Electrode

Metal and metal ion electrodes

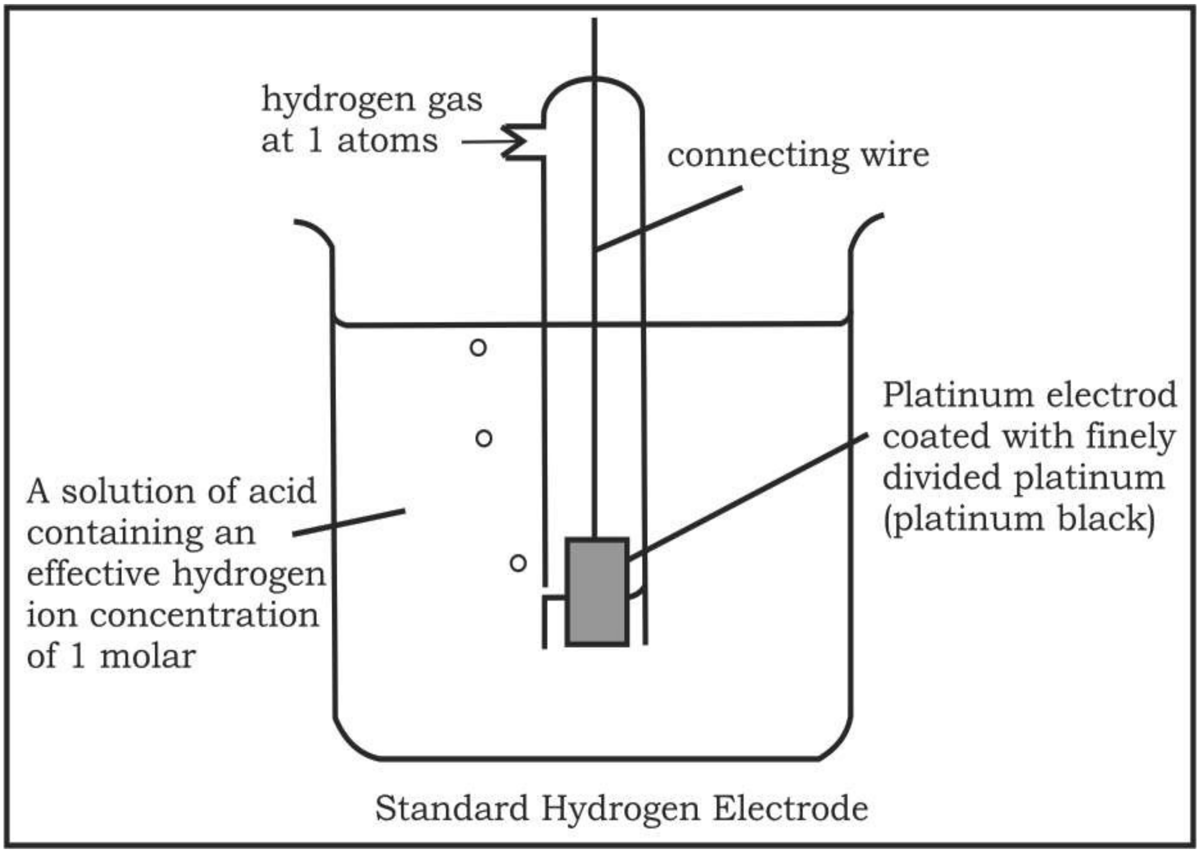
A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.

Anode: $M \longrightarrow M^{n+} + ne^{-}$

Cathode: $M^{n+} + ne^{-} \longrightarrow M$

Gas Electrodes

Electrode gases like H_2, Cl_2 etc are used with their respective ions. For example, H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.



Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

The hydrogen electrode is also used as the standard to measure other electrode potentials. Its own potential is set to 0 V as a reference. When it is used as a reference the concentration of dil HCl is taken as 1 M and the electrode is called "Standard Hydrogen Electrode (SHE)".

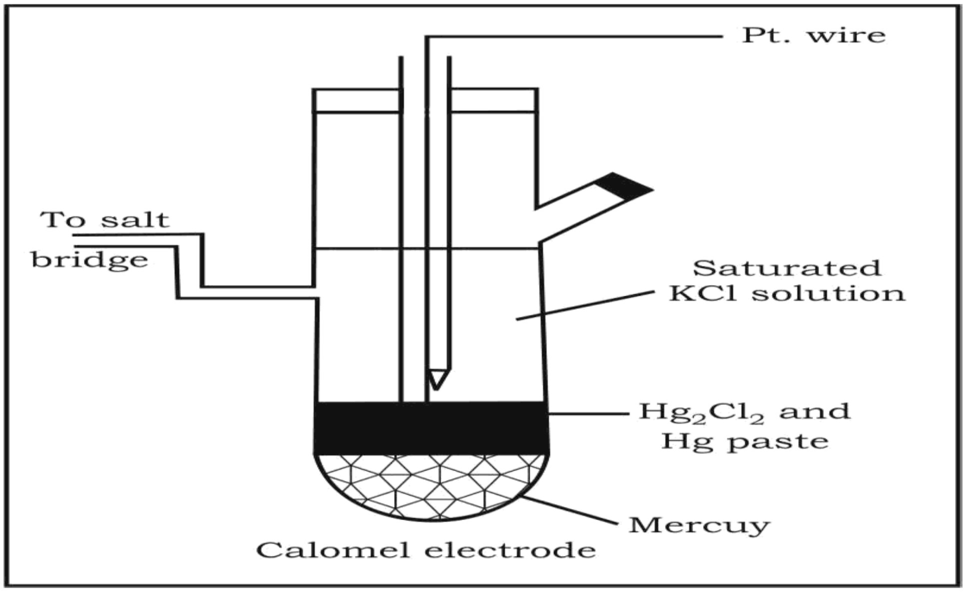
Metal- Insoluble salt Electrode

We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use AgCl with Ag there is a potential gap between these two phases which can be identified in the following reaction:

$$AgCl\ (s) + e^{-} \longrightarrow Ag(s) + Cl^{-}$$

Calomel Electrode

Mercury is used with two other phases, one is a calomel paste (Hg_2Cl_2) and electrolyte containing Cl ions.



Calomel electrode

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